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Mechanistic Studies on the Reaction of Alicyclic Ketones with Deuterium over Platinum Group Metals; Propagation of α,β-Process on Rh and Formation of π-Allylic Species on Pd

It is generally accepted that, of platinum group metals, Rh and Pd are most active for isotopic exchange in the reactions of alkenes or alkanes with deuterium (*1*). This is also the case in the reactions of ketones with deuterium (*2*), but there is a characteristic difference between Rh and Pd. In the reaction of cyclohexanone or its alkyl derivatives with deuterium over Pd, deuterium incorporation into the product alcohols was almost entirely limited to these four positions: O(xygen), C(1), C(2), and C(6), whereas deuterium smear beyond C(2) and C(6) was quite significant over Rh (*3*). A corollary of these results is that the adsorbed species responsible for deuterium exchange is π-allylic on Pd and α,β-diadsorbed on Rh. The deuterium smear on Rh is thought to occur by propagations of the α,β-process. Although the adsorption bonds on the α,β-diadsorbed species are in general considered to be eclipsed, we have previously (*4*) argued that the propagation of the α,β-process on Rh could occur via staggered α,β-diadsorbed species.

Owing to the rigidity of its molecular framework, adamantanone is unable to undergo any conformational change or tautomerization to the enol form. All vicinal pairs of C–H bonds on this ketone are thus held in the staggered conformation. Using adamantanone as a substrate for deuteration, therefore, it is possible to test whether the α,β-process based on the staggered α,β-diadsorption is operating. If it is not operating, deuterium entry in the product 2-adamantanol will be limited to the C(2) and O positions. If it is operating, however, deuterium must smear beyond these positions. We were prompted to put Rh and Pd catalysts to this test. For a better mechanistic understanding we also studied the isotopic exchange reaction of 2-adamantanol with deuterium.

Deuteration of adamantanone (1.0 g) was conducted using cyclohexane (20 ml) as the solvent in a 100-ml stainless-steel autoclave at deuterium pressures of 18–20 atm in a temperature range of 80–120°C. The catalysts (30 mg) were in the form of metal black. After reaction the reaction mixture was washed with ethyl alcohol and subjected to gas chromatography (column: 10% PEG 20M on Chromosorb WAW) to collect the product 2-adamantanol. The isotopic exchange reaction of 2-adamantanol was conducted under conditions similar to those for adamantanone deuteration. Deuterium distributions were examined by both mass spectrometry and NMR spectroscopy. NMR spectra were recorded with the aid of lanthanide shift reagent $Eu(dpm)_3$ (*5*).

The mass spectral data for the 2-adamantanol produced in adamantanone deuteration are listed in Table 1, which shows a striking contrast between Rh and Pd. On Pd, only d_1 was predominant. Since the hydroxyl deuterium has been washed away before mass and NMR spectral analysis, the preferential formation of d_1 suggests that deuterium entry was limited to the C(2) and O positions alone. In the case of Rh, the formation of not only d_1 but also d_2 was significant. There was even a small amount of d_3. These mass spectral results indicate that deuterium incorporation was not limited to C(2) and O. This has been further confirmed by the NMR data in Table 2 (Expts. 4 and 5), which indicates that the C(1) and C(3) positions were also deuterated.

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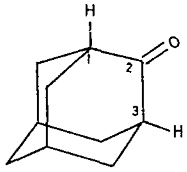
TABLE 1

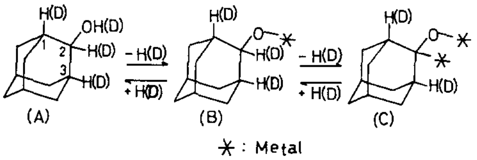
Isotopic Distributions Determined by Mass Spectrometry for 2-Adamantanol in Adamantanone Deuteration

Expt.	Cat.	Temp. (°C)	Conv. (%)	Percentage of isotopic species					D_m[a]
				d_0	d_1	d_2	d_3	d_4	
1	Pd	80	41	1.8	97.2	1.0	0	0	0.99
2	Pd	95	74	1.9	97.9	1.1	0	0	1.00
3	Rh	80	100	3.1	79.6	15.3	2.0	0	1.16
4	Rh	95	100	3.2	60.6	31.2	3.7	1.3	1.38
5	Rh	120	100	7.8	55.0	27.8	8.4	1.4	1.40

[a] Average number of D atoms per molecule.



The mass spectral data for isotopic exchange between 2-adamantanol and deuterium over Rh are compared with those over Pd in Table 3, and the NMR data on Rh are included in Table 2 (Expt. 7). The exchange on Rh was quite significant, forming a considerable amount of d_1 and a small amount of d_2 species, whereas the exchange on Pd was almost negligible. The NMR data (Expt. 7, Table 2) reveal that over Rh deuterium incorporation is concentrated at the C(2) position. These exchange data obtained for Rh are also compatible with the concept of the α,β-process. The exchange process is likely to start with dissociative adsorption of 2-adamantanol (A) to form adsorbed species (**B**), in which the most versatile hydroxyl hydrogen is lost. (**B**) could be converted to the C(2), O-diadsorbed species (**C**).



The observed significant deuterium incorporation at C(2) is accounted for by interconversion between species (**B**) and (**C**). Once species (**C**) is formed, then deuterium incorporation into C(1) and C(3) may be feasible by the α,β-process. The observed appearance of d_2 (Expt. 7, Table 3) is thus accounted for.

In conclusion, the results outlined above are exactly what we expected on the basis of the propagation of the α,β-process for Rh and the formation of π-allylic species

TABLE 2

Isotopic Distributions Determined by NMR for 2-Adamantanol

Expt.	Cat.	Temp. (°C)	D_c[a]			D_m
			C(2)	C(1) + C(3)	C(4) + C(10)	
4	Rh	95	1.00	0.35	0	1.35
5	Rh	120	1.00	0.38	0	1.38
7	Rh	80	0.20	0	0	0.20

[a] Average number of D atoms at each carbon position.

TABLE 3

Isotopic Distributions for 2-Adamantanol Determined by Mass Spectrometry in Exchange with D_2

Expt.	Cat.	Temp. (°C)	Time (min)	Percentage of isotopic species				D_m
				d_0	d_1	d_2	d_3	
6	Pd	80	420	99.3	0.7	0	0	0.00_7
7	Rh	80	450	73.4	23.0	3.6	0	0.30

for Pd, thereby providing further evidence for a unique process on each metal.

ADDENDUM

A referee has made three comments on this article. In the first comment he points out some risk of extrapolating the mechanistic argument from somewhat hindered adamantanone to simpler ketones. In the second comment he refers to the possibility that the hydrogen atom at C(1) on adamantanone may have exchanged before hydrogenation. These possibilities, we admit, are not completely deniable. The exchange mechanisms proposed here are consistent with, but not verified by, the presented exchange data.

As his last comment, in conflict with our proposed mechanism, the referee suspects that dissociative adsorption of 2-adamantanol involves cleavage of the O–H bond. As support for this suspicion he refers to the data for $C_4H_8 + D_2$ in Ref. (*6*), and also points out that the dissociation energy for the O–H bond [E_d(O–H)] is substantially larger than that for C–H [E_d(C–H)]. We believe that this is valid only for isolated alcohol molecules, but not for those alcohol molecules that are mutually attracted by the hydrogen bond. In the latter situation, the O–H bond must be much elongated and weakened, thus giving rise to the reverse relationship.

$$E_d(\mathrm{O{-}H}) < E_d(\mathrm{C{-}H}).$$

This is compatible with the well-known facts that not the C–H but the O–H hydrogen is amenable to exchange when an alcohol is brought into contact with D_2O. It is to be noted that the experiments in Ref. (*6*) were done in the gas phase, while our deuteration and exchange were conducted in cyclohexane solutions where hydrogen bonding between 2-adamantanol molecules is expected.

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